

THE INITIAL CHEMICAL EVENTS IN CL-20 UNDER EXTREME CONDITIONS: AN *AB INITIO* MOLECULAR DYNAMICS STUDY

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ABSTRACT

CL-20 (Octahydro-1,3,4,7,8,10-hexanitro-5,2,6-(iminomethenimino)-1H-imidazo[4,5-b]-pyrazin, C₆H₆N₁₂O₁₂), is an emerging energetic chemical that may replace RDX, however its degradation pathways are not well-known. In the present study molecular structure, electrostatic potential, vibrational spectrum and dynamics of thermal decomposition of CL-20 have been investigated by static and dynamic methods of ab initio computational chemistry. Based on good corresponding between predicted and computed data we concluded that the results of computational chemistry calculations can be used to guide predictions of the chemical behavior and degradation pathways of emerging contaminants in the environment.

1. INTRODUCTION

CL-20 (Octahydro-1,3,4,7,8,10-hexanitro-5,2,6-(iminomethenimino)-1H-imidazo[4,5-b]-pyrazin) belongs to one of the most important classes of high energetic compounds – nitramines. It has been first synthesized in 1987 (Nielsen et al., 1998) and was applied by military and industry. It releases large amounts of energy through a bulk decomposition process that has been considered as rather complex and involving both unimolecular and bimolecular reactions. Among the experimental investigations performed in this area we would like to recognize the one which include the studies of synthesis pathways (Nielsen et al., 1998; Clawson et al. 2004), properties (Monteil-Rivera et al., 2004; Sorescu et al., 1999; Sikder et al., 2001) and different methods of CL-20 decomposition (Balakrishnan et al., 2003; Qasim et al., 2005; Bhushan et al., 2004; Hawari et al., 2004; Szecsody et al., 2004). In particular, it was established the existence of four CL-20 polymorphs and they have been studied (Foltz et al., 1994; Politzer 1991). Fourier Transform Raman Spectroscopy has been used to characterize these stable phases of CL-20 (Goede et al., 2004). Stewart (1989), Dewar and Theil (1997) have calculated the geometric structures of CL-20 using semi-empirical AM1 and PM3 methods. Conformations of CL-20 have been investigated by Zhou et al. using the DFT level of theory (2002). The heats of detonation of pure CL-20 have been calculated by means of quantum-mechanical calculations

by Rice and Hare (2002). Degradation pathways for CL-20 (Qasim et al., 2004; Okovytyy et al., 2005; Qasim et al., 2005) as well as for simpler cyclic nitramines, such as dimethylnitramine (Johnson, 1999), hexhydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Chakraborty et al., 2000; Long et al., 2000), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (Chakraborty et al., 2001; Zhang, 2003; Lewis et al., 2000; Manaa, 2002) have been also predicted using *ab initio* levels of theory. Based on the obtained results of experimental and theoretical investigations one may conclude that the decomposition of CL-20 is very complex and involves hundreds of elementary reactions. Accurate knowledge of these reactions and predictions of their energetic parameters are important for modeling these complex processes in combustion and explosion. However, due to the energetic nature of these materials and the rapid rates of the intermediate reactions, it is difficult to monitor these individual reactions experimentally. Recent advances in first principles modeling have led to enormous progress toward understanding complex condensed phase chemical phenomena. Theoretical methods, especially accurate ab initio static and molecular dynamics method, provide a viable alternative to study the dynamics of these reactions.

In the paper we present the results of our study of molecular and electronic structure and decomposition pathways of CL-20. All calculations were performed using reliable non-empirical methods of computational chemistry.

2. COMPUTATIONAL DETAILS

Ab initio and DFT calculations have been performed with the program GAUSSIAN03 (Frisch et al., 2004). The fully optimized geometries of studied compounds have been calculated with 6-31G(d) basis set at the hybrid Becke3/Lee–Yang–Parr (B3LYP) (Becke, 1993) levels of theory. The minima of the potential energy surfaces have been found by relaxing all the geometric parameters with standard optimization methods. Analytical force constants have been derived at the same level of theory. The software package SPECTRUM (Yagola et al., 1999) has been used for transformation of quantum mechanical Cartesian force constants to the matrix in redundant internal coordinates with minimal off-diagonal norm

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(Kuramshina et al., 1994). Normal coordinate analysis for all investigated molecules and potential energy distribution (Kerestury, 1971) (PED, %) calculation have been also carried out using SPECTRUM.

To reduce differences between calculated and experimental data, the predicted B3LYP/6-31G(d) vibrational frequencies have been scaled to account for various systematic errors in the theoretical approach, i.e., the use of a finite basis set, the neglect of vibrational anharmonicity, and the incomplete account for electron correlation effects. All predicted frequencies have been scaled with a uniform scaling factor 0.9806 (Scott and Radom, 1996).

The Car-Parrinello molecular dynamics simulations (Car and Parrinello, 1985) were performed with the CPMD program (CPMD 3.9.1. Copyright IBM Corp 1990-2005) using a plane-wave basis and BLYP functional (Becke, 1988, Lee et al. 1988). The wave function was expanded at the point in a plane-wave basis set with the kinetic energy cutoff of 70 Ry and 120 Ry respectively. A large 18 Å cubic box was used under the periodic boundary conditions (Martyna et al., 1999) to prevent the interaction between the periodic images.

The form of the nonlocal pseudopotential according to Kleinman and Bylander was employed (Kleinman and Bylander, 1982), and the core electrons were described by the Trouiller and Martins pseudopotentials (Troullier and Martins, 1993). The timestep 5 a.u. (where 1 a.u. = 0.0241888 fs) was used for the numerical integration of the equations of motions, according to the velocity Verlet algorithm. In order to determine the properties averaged within the canonical ensemble, a Nose-Hoover chain thermostat (Martyna et al. 1992) with a length of 4 and a characteristic frequency of 500 cm⁻¹ was used on the nuclear degrees of freedom. For the calculation of the crystal-phase CL-20 a monoclinic unit cell with dimensions 13.596, 8.384, 15.320 Å was used. Continuous trajectories of 7-10 ps were obtained in the NVT ensemble. The temperatures were set to 1500 and 3000 K.

3. RESULTS AND DISCUSSION

3.1. Static ab initio calculations

The molecular structure of CL-20 molecule is presented in Figure 1. The basic structure of CL-20 consists of a rigid isowurtzitane cage, which includes two five-member rings and a six-member ring. Two five-member rings link each other by the C-C bond at the top and project outwards at two pairs of N-atoms. This bond is an important stabilization factor. There is considerable tension in the skeleton of the studied compound. The six-member ring is boat-shape with the prow directed downwards. The CL-20 molecule has six nitro groups attached to each of the six bridging nitrogen atoms in the cage.

The spatial orientation of the nitro groups has little influence on the skeleton. The N-N bonds of CL-20 are more fragile than its other bonds. All spatial orientations of these nitro groups with respect to the five-member rings and the six-member ring in the cage, the differences in crystal lattice packing, and the number of molecules per unit cell define four possible polymorphs [16-18,23]. Among them we have considered only the most stable conformation of CL-20 which is presented in Figure 1.

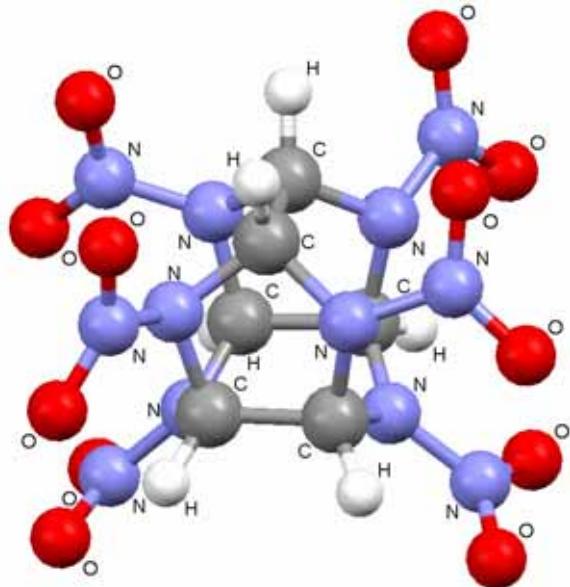


Fig. 1 Molecular structure of CL-20 molecule

Taking into account the highly strained bonding pattern of the CL-20 molecule on one hand and the similar chemical structure with those of the RDX and HMX molecules on another hand one would suggest that initial transformation reactions could be also similar in RDX, HMX [9] and CL20. Additional evidences for this statement could be obtained analyzing the distribution of electrostatic potentials (ESP) for the all considered molecules which are presented on Figure 2.

Indeed, an analysis of the information presented in Figure 2 suggests very comparable reactivity of all considered species due to their similar ESP distribution. Namely, the concentration of negative electronic charge in the area of nitro-groups and positive electronic charge for the rest of the heterocycle backbone. Therefore, it could be expected that after initial transformations, the reactions products of CL-20 would degrade following the pathway of the other nitramines [38-41].

Regardless of method used for CL-20 degradation, the problem of products identification is of vital importance due to the toxicity and potential carcinogenicity of this compound and its transformation products. IR spectroscopy is a valuable tool to identify different chemicals and the products of their reactions. Therefore, we have predicted the harmonic vibrational

spectrum of CL-20 (see Figure 3). The optimized at the B3LYP/6-31G(d) level equilibrium configuration of CL-20 molecule in the ground state belongs to the C_2 symmetry point group. This molecule has 36 atoms that give rise to 102 normal vibration modes distributed among symmetry elements according to: $52A + 50B$. All

vibrations are active in the IR spectrum. The redundant system of internal coordinates for this molecule includes a totally of 138 coordinates: 39 for bond stretchings, 55 for bond angles, 23 for out-of-plane bendings and 21 torsional coordinates.

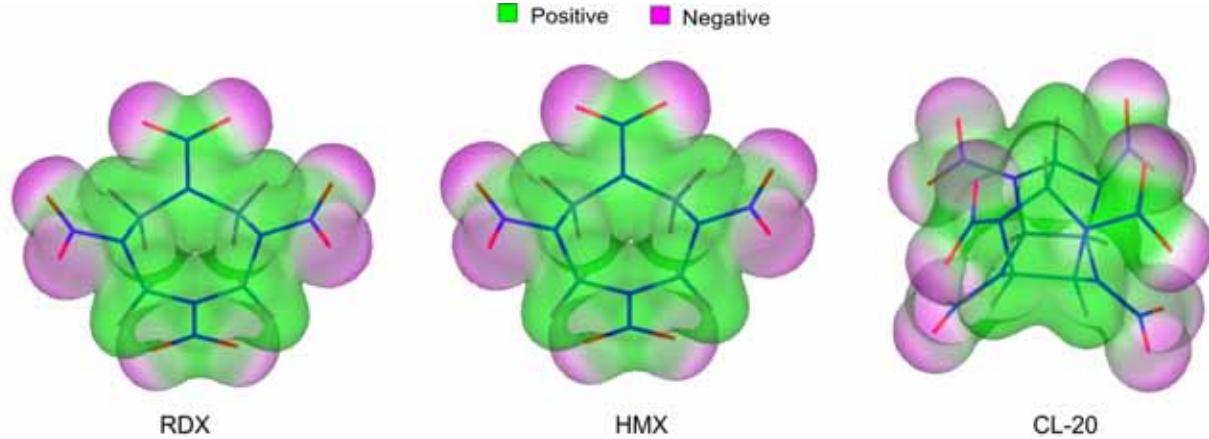


Fig. 2. Electrostatic potential distribution for CL-20.

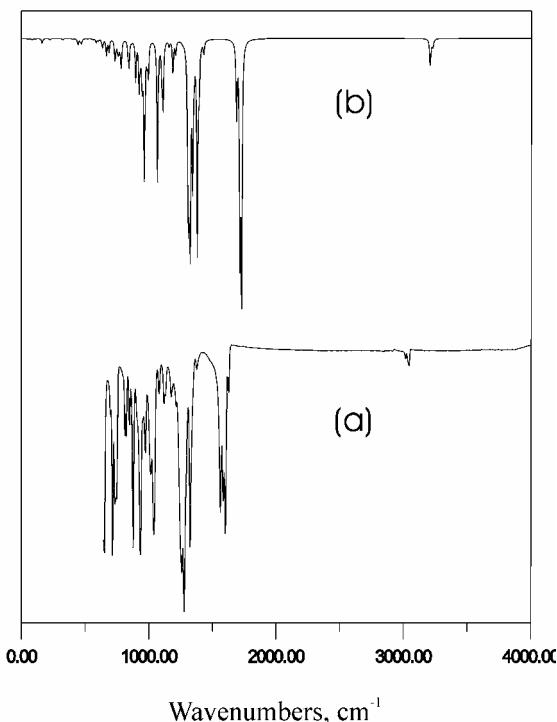


Fig. 3. The experimental (a) and the predicted at B3LYP/6-31G(d) level of theory (b) Infrared spectra for CL-20.

The symmetry coordinates have been constructed automatically by means of the SYMM utility included in SPECTRUM.

The comparison of the theoretical and experimental spectrum presented in Figure 3 suggests that selected scaled theoretical frequencies remain slightly overestimated, especially for the nitramine groups. Possibly, used uniform scaling factor is not sufficient for the accurate correction of all theoretical frequencies. Moreover, it is necessary to take into account that we have compared the theoretical results obtained for the gas phase and experimental spectra have been registered for the condensed state, which should be differentiated from the gaseous state spectra. Nevertheless the calculated and the experimental IR spectra of CL-20 are in a good agreement for the most of frequencies in the considered IR region. The main features of the observed IR spectrum are satisfactorily reproduced by calculation both for the positions and intensities of IR bands. A group of low intensity theoretical modes assigned to the CH-stretchings within $3166\text{-}3140\text{ cm}^{-1}$ region can be assigned to a weak double peak at $3043\text{-}3016\text{ cm}^{-1}$. The well-known fact is that among three stretchings of nitramine group ($\nu^{as}(NO_2)$, $\nu^s(NO_2)$, $\nu(N-N)$) only $\nu^{as}(NO_2)$ can be considered as approximately characteristic and used in analytical investigations. For CL-20 the calculated asymmetrical NO-stretchings are located near $1690\text{-}1652\text{ cm}^{-1}$ (corresponding experimental bands in IR spectrum of CL-20 are observed at $1605\text{-}1566\text{ cm}^{-1}$). These vibrations are characteristic both by position and PED.

Calculations predict three stretchings of the six-member ring represented by three bands of low or moderate intensity at 1261 , 1183 and 971 cm^{-1} . In the experimental IR spectrum there is a shoulder at 1219 cm^{-1} and a weak band at 1180 cm^{-1} which can be considered as

corresponding to these vibrations. Two groups of frequencies at 1190-1155 cm⁻¹ (moderate bands) and at 901-875 cm⁻¹ (strong bands) in theoretical spectrum of CL-20 are related to stretchings of five-member rings. They can be assigned to a shoulder at 1138 cm⁻¹ and a strong peak at 883 cm⁻¹ in the experimental spectrum. Calculated in-plane deformation vibrations of the five-member rings and the six-member ring are very close to experimental values: 973 vs. 980 cm⁻¹ for the five-member rings and 942 vs. 941 cm⁻¹ for the six-member ring. Bands connected in-plane deformation vibrations of with the six-member ring are of moderate intensity while corresponding peaks of the five-member rings have high intensity.

According to calculations, NN-bond stretching vibrations result in several moderate and strong peaks in the frequency area of 1087-1043 cm⁻¹ as well as a strong peak at 875 cm⁻¹. These vibrations are observed experimentally as moderate and strong bands at 1126-1045 and 856 cm⁻¹. According to calculations C₁C₁₀-bond stretching is located at 962 cm⁻¹ and has a moderate intensity. The six-member ring breathing-like deformation of small intensity is predicted near 829 cm⁻¹. The observed IR spectrum in this region has rather complicated structure with a series of overlapping bands and we can only very tentatively compare this region of experimental and theoretical spectra. So the listed above two modes could be approximately compare to bands between 980 and 829 cm⁻¹. Theoretical bending modes of ONO-groups appear as three bands of low or moderate intensity at 812, 804 and 730 cm⁻¹ and are obviously located near experimentally observed shoulder at 706 cm⁻¹. The lowest band registered in observed IR spectrum located at 660 cm⁻¹ can be assigned as a mixed NN-bond stretching and deformation mode. It corresponds to a theoretically estimated moderate band at 650 cm⁻¹.

3.2. Dynamics ab initio CPMD simulations

First, the effect of the unit cell length was tested by expanding the box size to about 20 Å. Only a minor variation of the total energy was found. Basing on these data the simulation of pathways of initial CL-20 decomposition was performed in the box having the size of 18 Å. One of the obtained snapshots of such decomposition is presented on Figure 4.

The general outline of the initial steps of unimolecular decomposition of CL-20 is follows:

During the first 100 fs all nitro groups cleave one by one. As soon as two-three NO₂ groups are eliminated the concerted ring fission proceeds. By the period 0.3-0.4 ps the ring essentially brakes down to three-six pieces and all NO₂^{*} flown away. This starts various branching reactions e.g oxidation on carbon to aldehyde by NO₂^{*} radical; migration of proton-radical; decomposition of NO₂^{*}. Under temperature T = 1500 K the reaction is slower, however, the situation is almost the same except for the

one aspect. Under this temperature there is much higher probability of HONO elimination. It is in contrast to 3000 K runs, where this reaction has not been observed. After several picoseconds of the dynamics of isolated CL-20 the NO₂ and HCN in quantities 5 and 3 molecules (per one initial molecule of CL-20) are founded to be the major products of its decomposition.

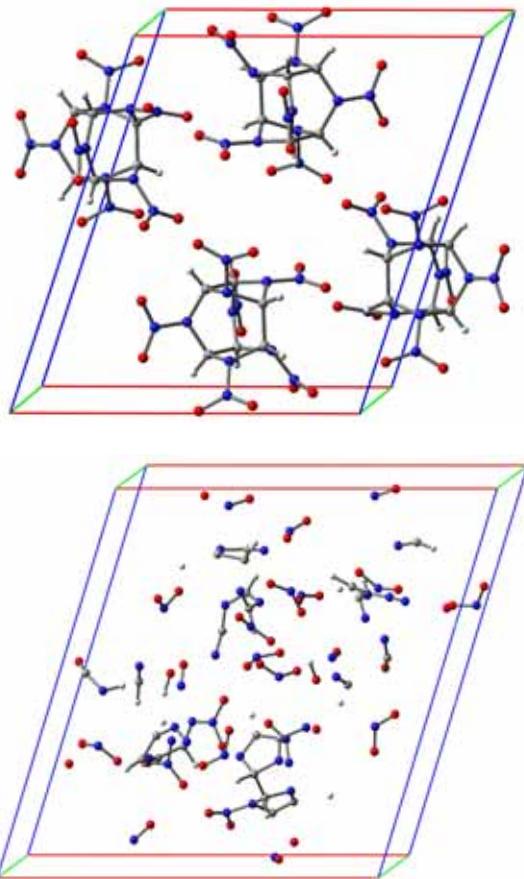


Fig. 4. Snapshots of crystal phase decomposition at 3000 K

The dynamics of crystal phase is much more complicated and diverse. Because of higher density and many immediate neighbors the NO₂ groups are eliminated slowly and immediately start to participate into various reactions. Even by the 0.5 ps time period there are few NO₂ or NO groups connected to the fragments of CL-20 ring. In addition various reaction products are formed: N₂O, NO, various aldehydes and heterocyclic compounds. The amount of formed HCN is lower than in the gas phase. Even after two picosecond runs large polyatomic molecules from the ring decomposition still exist.

CONCLUSIONS

Systematic study of the geometrical structure, electrostatic potential, vibrational spectra and

decomposition pathway at 1500K and 3000K for 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaazatetra-cyclo-[5.5.0.0^{5,9}.0^{3,11}]-dodecane, 1,5- and 1,7-dihydro-diimidazo[4,5-b:4',5'-e]pyrazine has been carried out at using static and dynamic ab initio techniques of computational chemistry. The good correspondence between computationally predicted and available experimental data suggests the significance of computational chemistry as the tool which can supplement or even substitute experimental measurements.

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